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A STUDY OF THE DEGRADATION OF METHOMYL (LANNATE) IN AND ON THE LEAVES, HUSKS AND SILK OF SWEET CORN AND THE SOIL IN A FIELD IN YOLO COUNTY, CALIFORNIA JULY 1976

By

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Methomyl is a toxic carbamate insecticide. Methomyl has an acute oral LD_{50} (rats) of 17 mg/kg and a dermal LD_{50} of greater than 5000 mg/kg.

Methomyl is registered for broad spectrum control of insects on many vegetables, field crops, certain fruit crops and ornamentals. It is marketed under the trade names of Lannate and Nudrin in two formulations, a 90% water-soluble powder and a liquid containing 1.8 lbs. methomyl per gallon.

This study deals with the water-soluble powder. Label directions allow 1/4 to 1/2 lbs. of Lannate on sweet corn with no preharvest interval on the ears and a 3-day preharvest interval if the corn is to be used for forage. There is a tolerance of 10 ppm on forage and fodder and a 0.1 ppm tolerance on the fresh grain. There was a 24-hour worker safety interval in effect when this study was done.

APPLICATION AND SAMPLING

An 84-acre corn field was treated with 1/2 pound of Lannate (0.45 lbs. actual methomyl), and 1/2 pint mevinphos (Phosdrin) in 10 gallons of water per acre. The Phosdrin breakdown has been reported in a separate study. Application was made by aircraft.

Triplicate leaf samples were taken at 5, 29, 51, and 75 hours post-application. Samples were collected at a diagonal across the field. Each leaf sample consisted of approximately 100 leaf discs, 2.5 cm in diameter. Two of the three samples were analyzed for surface and penetrated residue while the third was for total residue analysis.

Six ears of corn were collected along the same diagonal path for analysis of silk and husk residue. Samples were taken at the same interval as leaf samples.

Surface soil samples were collected twice during the study. They were taken along the same diagonal path.

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ANALYTICAL METHODS (Extraction from Leaves)

The procedure used for the extraction of dislodgeable, penetrated, and total residues from leaf punches was originally published by Gunther in "The Bulletin of Environmental Contamination and Toxicology," 9, 243-249, 1973. It has been documented several times in detail, with modifications that were made to accommodate the various pesticides and their metabolites, that our Worker Safety Unit has been concerned with.

The sample container and leaf punches were weighed and the gross weight recorded.

Total Residues

1. The leaf punches were transferred to a blending jar. The empty sample container was again weighed and the net weight of the punches recorded.

2. Approximately 50 gms of sodium sulfate and 100 mls of ethyl acetate were added.

3. The sample was blended at high speed for 3 minutes, keeping the blender cup cool by immersing it in a container of cool water. The blender cup was removed and the sample allowed to settle.

4. An aliquot was decanted into a teflon-capped bottle and stored in the freezer prior to clean up and analysis.

Dislodgeable Residues

1. Fifty mls of water and approximately 4 drops of Sur-Ten solution (1:50) were added to the sample containers. The containers were capped and placed in a multi-purpose rotator and rotated at 30 cycles/min. for 60 min. The aqueous solution was decanted through a glass plug into a 500 ml separatory funnel.

2. The punches were rotated a second time, using 50 mls of water and 4 drops of Sur-Ten solution, for 30 min. This was added to the first extraction.

3. The sample was then hand-shaken for approximately 10 secs with 30 mls of water. The container was drained into the separatory funnel with the first two extractions.

4. The aqueous solution was extracted three times with 50 ml of ethyl acetate. The extract was filtered through sodium sulfate into a glass-stoppered mixing cylinder and the volume was recorded. The extract was mixed in the cylinder. An aliquot was decanted into a teflon-capped bottle and stored in the freezer prior to clean-up and analysis.

Penetrated Residue

1. After the last water rinse was drained for the dislodgeable residue, the punches were transferred to a blender jar. The empty sample container was weighed and the net weight of the punches recorded.

2. Approximately 50 gms of sodium sulfate and 100 mls of ethyl acetate were added.

3. The sample was blended and handled the same as the total residue sample.

ANALYTICAL METHODS (Extraction from Silk and Husks)

1. The silk and husk samples were transferred to a blending jar. The empty sample container was weighed again and the net weight of the punches recorded.

2. Approximately 50 grams of sodium sulfate and 100 mls of ethyl acetate were added.

3. The sample was blended at high speed for 3 minutes, keeping the blender cup cool by immersing it in a container of cool water. The blender cup was removed and the sample was allowed to settle.

4. An aliquot was decanted into a teflon-capped bottle and stored in the freezer prior to clean-up and analysis.

ANALYTICAL METHODS (Extraction from Soil)

1. The soil sample was finely divided to remove or break up lumps. It was air dried if muddy.

2. 10% water by weight was added and it was mixed well.

3. The sample was extracted with a 2:1:1 petroleum ether: ethyl ether: acetone mixture. The maximum amount compatible with the sample container was used so that there was free liquid over the soil.

4. The sample was placed on the jar-rotator or shaker for 1 hour.

ANALYTICAL METHODS (Clean-up)

1. The sample was transferred to a 25- ml separatory funnel. The flask was rinsed with 50 ml 0.01 N H_2SO_4 and this was added to the separatory funnel. The flask was rinsed with 50 ml of water and this was added to the funnel.

2. This was agitated gently for 1 min. Vigorous agitation will cause emulsions. Insufficient agitation will result in low recoveries.

3. After phase separation, the ethyl acetate was discarded. The ethyl acetate partitioning was repeated if necessary. Multiple extractions do not depress recoveries.

4. The aqueous layer was extracted 3 x 50 with CH_2Cl_2, drying each extract with sodium sulfate.

ANALYTICAL PROCEDURES (Chromatography)

For liquid-chromatographic determination, an appropriate volume was concentrated and injected.

LC Conditions:

Chromatronix 3500, Schoeffel detector at 223 nm
Partisil 10 micron column 25 cm long
6% MeOH in ethyl ether at 2 ml/min

Retention time:

Lannate - 5 minutes

RESULTS

Daily temperature and weather conditions are recorded on Table 1. The average maximum and minimum termperatures during the study period were 94.4 and 60.2 °F, respectively.

The results of the analysis are recorded on Tables 2-4 and on Figure 1-2. Methomyl on leaves showed a steady rate of decline, so that in 75 hours the total residue had nearly reached 10 ppm. No methomyl was detected in the husks in 75 hours, while residue on the silk was still about 3.5 ppm.

TABLE 1: DAILY TEMPERATURE AND PRECIPITATION

Date (1976)	Temperature (°F) Maximum	Minimum	Conditions	Precipitation
7/19	89	60	Clear	0
20	95	58	Clear	0
21	92	58	Clear	0
22	98	59	Clear/cloudy	0
23	98	66	Cloudy/clear	0
Average	94.4	60.2	Clear	0

TABLE 2: METHOMYL RESIDUE ON SWEET CORN LEAVES

Date (1976)	Sample Number	Sample Interval	Methomyl Residue (PPM) Surface	Penetrated	Total
7/20	1	5 hrs	27.2	13.2	
20	2	5 hrs	33.98	18.0	
20	3	5 hrs			72.4
21	4	29 hrs	Sample lost	Sample lost	
21	5	29 hrs	20.0	5.72	
21	6	29 hrs			30.5
22	8	51 hrs	Sample lost	Sample lost	
22	9	51 hrs	14.4	6.1	
22	10	51 hrs			18.3
23	11	75 hrs	Sample lost	Sample lost	
23	12	75 hrs			10.2
23	13	75 hrs	9.96	0.94	

TABLE 3: METHOMYL RESIDUE ON SILK AND HUSKS OF SWEET CORN

Date (1976)	Sample Number	Sample Interval	Total Methomyl Residue (PPM)	
			Silk	Husk
7/20	1	5 hrs	2.45	2.26
21	2	29 hrs	4.85	1.68
22	3	51 hrs	4.77	1.21
23	4	75 hrs	3.47	None detected

TABLE 4: METHOMYL RESIDUE IN SOIL OF SWEET CORN FIELD

Date (1976)	Sample Number	Sample Interval	Total Methomyl Residue (PPM)
7/20	1	5 hrs	30.4
22	2	51 hrs	4.91

FIGURE 1: METHOMYL RESIDUE ON SWEET CORN LEAVES
YOLO COUNTY, CALIFORNIA JULY 1976

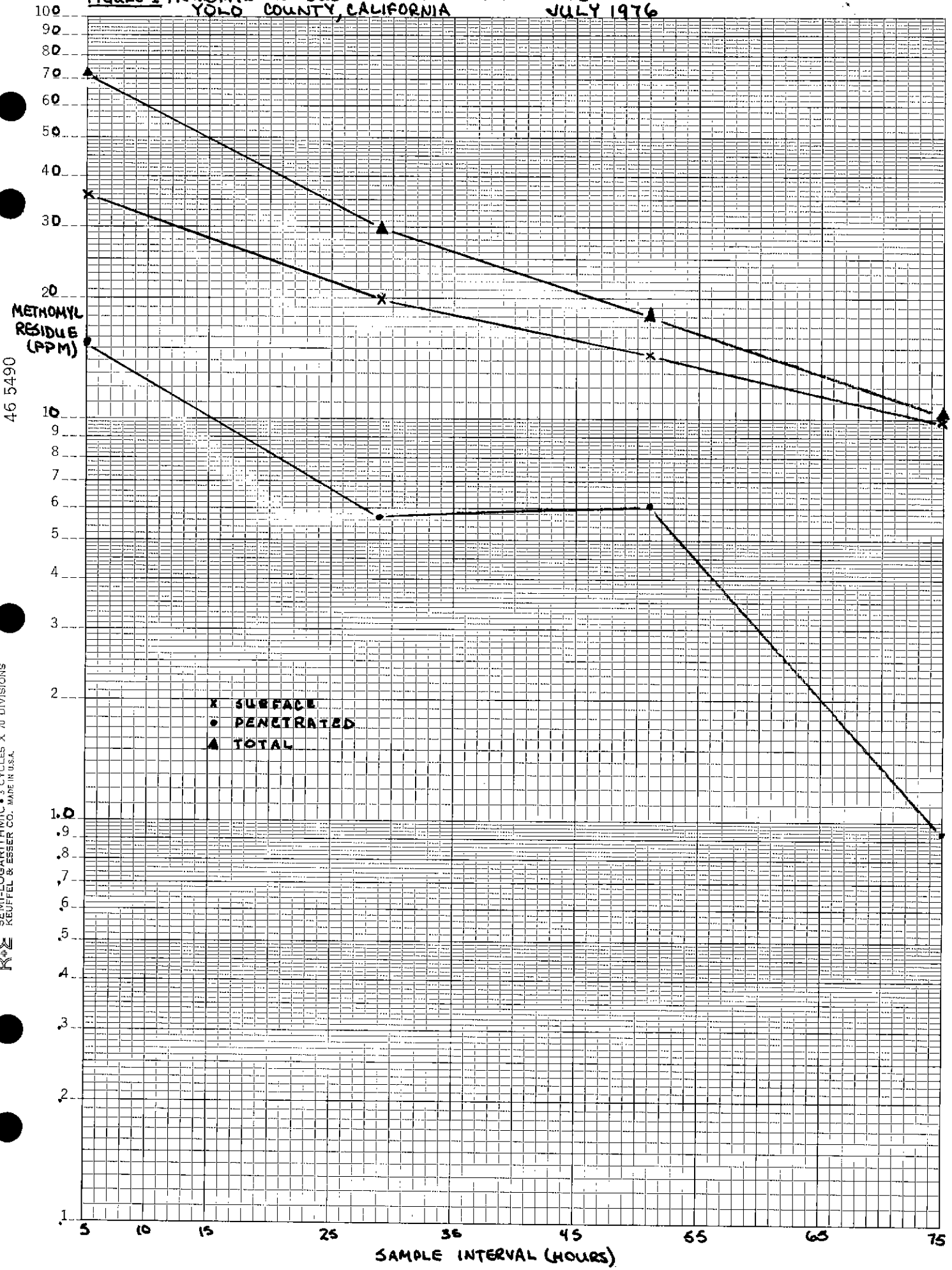

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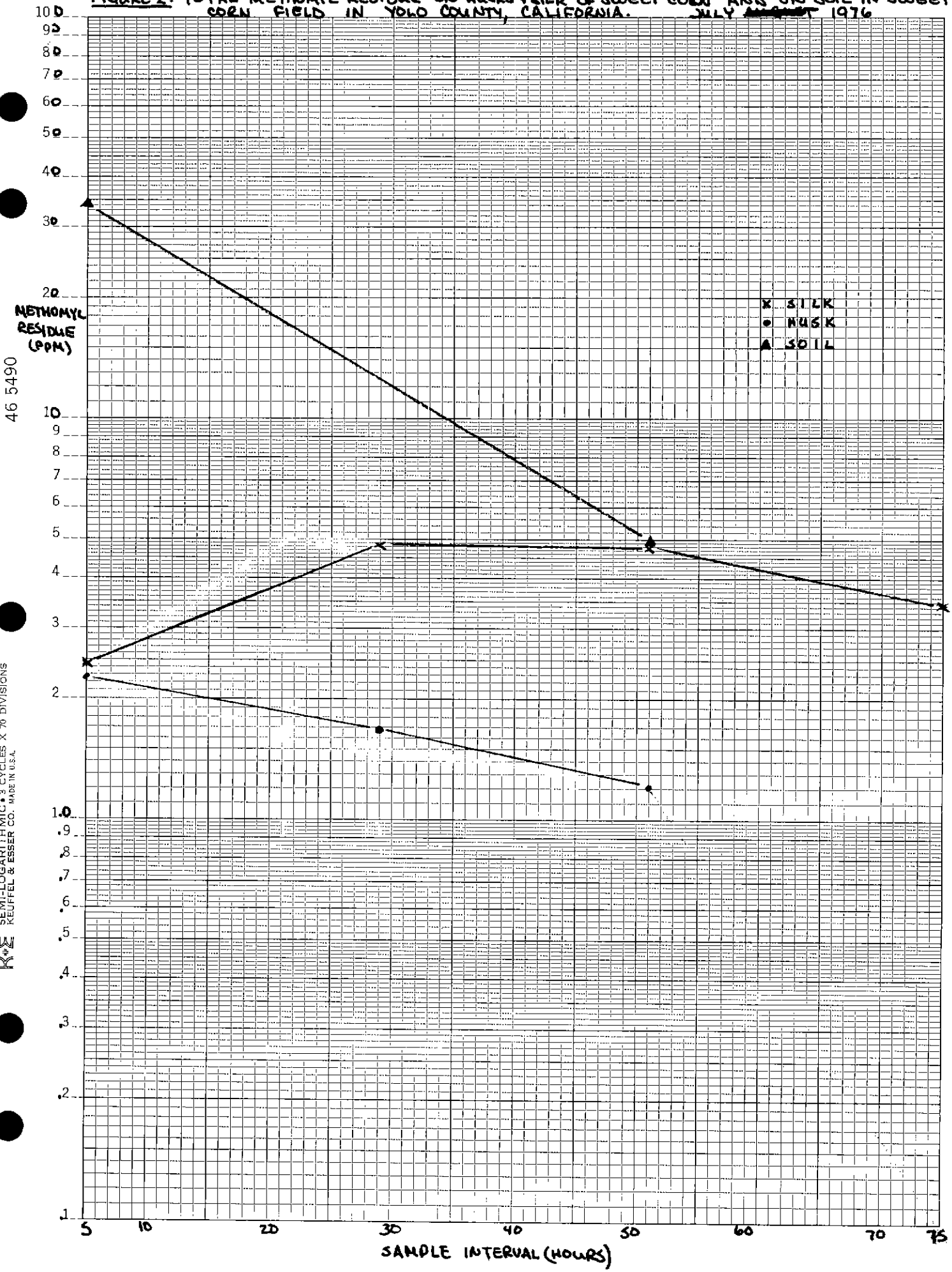
FIGURE 2: TOTAL METHOMYL RESIDUE ON HUSKS & SILK OF SWEET CORN AND ON SOIL IN SWEET CORN FIELD IN YOLO COUNTY, CALIFORNIA. JULY ~~AUGUST~~ 1976



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